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RESEARCH AND DEVELOPMENT ON THE EFFECTS OF HIGH PRESSURE  
AND TEMPERATURE ON VARIOUS ELEMENTS AND BINARY ALLOYS

by

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ABSTRACT

An investigation has been made of the effect of pressure on the properties and kinetics of transformation in various alloy systems. Many of the experiments were exploratory and yielded no evidence for irreversible changes with pressures of up to 100,000 atm at elevated temperatures. However, a shift was observed in the gamma loop of the iron-chromium system from 12.5 to about 20 per cent chromium. Evidence for a similar shift in the gamma loop of the iron-aluminum system was also found. Pressure heat treatment of a tool steel gave a refinement of the austenite grain size and an improvement in the distribution of carbides.

I. INTRODUCTION

The purpose of this project was to study the effects of the application of high pressure and temperatures on selected elements and binary alloys to determine whether new metallic structures of existing alloys or wholly new alloys can be produced. The program was designed to be exploratory in nature. Some of the studies dealt with metals and alloys that were of interest as structural materials whereas other studies dealt primarily with mechanisms and the alloys involved were of secondary interest.

The more important conditions and mechanisms which were considered in selecting alloy systems for study under pressure are given below. In some cases there was little-known theoretical basis for expecting that these desired changes would occur.

1. Lattice transformations which are likely to occur under pressure such as the transformation from body-centered cubic to the denser face-centered cubic structure.
2. Changes in solubility which might occur under pressure.
3. Suppression of undesirable phases and the favoring of desirable phases under pressure.

4. Systems in which alloying is predicted by relationships such as atomic sizes, crystal structures, etc., but where alloying is difficult to effect at atmospheric pressure because of the volatility of one component. In these systems extremely high pressures may not be necessary to contain the components.

5. Atom compressibility as indicated from considerations of atomic structure and/or experimental work of P. W. Bridgman.<sup>(1)</sup>

This phase of the program was designed to uncover primarily nonreversible changes, but it should be noted that the products of some reversible changes would have been detected by the studies made. Thus, increased solubility under pressure, even though reversible, might be indicated by the presence of a fine dispersion or precipitate. Such a result, of course, might prove quite valuable. Furthermore, the compressing of an atom itself would appear to be almost certainly reversible, but nonreversible structural modifications might have been attained by temporarily compressing atoms of one variety.

The high pressure equipment employed had been in use in the High Pressure Laboratories of the Metallurgical Products Department and in the Research Laboratory of General Electric Company, and no effort was expended as a part of this contract in modifying the basic design of the apparatus. Experiments were conducted up to pressures of 100,000 atmospheres and temperatures to 2500°C.

The experimental results are grouped according to the nature of the changes anticipated and not in the order in which the experiments were conducted. Because of the availability of materials and special equipment required and because of the limited time for the program it was considered advisable to run many of the experiments simultaneously. It was felt that this would not detract seriously from the results obtained since the individual studies were exploratory in nature and relatively brief. By so proceeding it was possible to explore a larger number of systems in minimum time, but it should be recognized that some obvious refinements should have been made and would have been made had the runs been made sequentially.

## II. EXPERIMENTAL PROCEDURE

As previously noted, the pressure apparatus employed is capable of attaining at least 100,000 atm and temperatures in excess of 2000°C. Originally, it was planned to carry out experiments at 50,000 atm pressure at a suitable temperature, and at holding times of up to 5 minutes so as not to cause undue strain on the pressure apparatus. Sample size was 0.375 inch in diameter x 0.500 inch long. However, as early experiments proceeded, several pressure vessel failures occurred, and in an attempt to remedy the situation the sample diameter was reduced to 0.200 inch and the thickness of the liner material correspondingly increased. This modification proved so successful that later experiments were extended to 100,000 atm and time at temperature was frequently extended to 30 minutes with no difficulty. In an effort to retain products of high pressure-temperature treatments all specimens were quenched under pressure by removing power under pressure and utilizing the apparatus as a heat sink. In most cases, specimens had cooled to less than 200°C within 60 seconds after power removal.

Al<sub>2</sub>O<sub>3</sub> was the principal ceramic liner material used. In cases where extensive reaction occurred between the specimen and the liner material, such as occurred in alloys containing titanium, MgO was employed with good success.

Sample temperature during a pressure run was measured by means of a Pt/Pt-Rh thermocouple encased in a fired alumina tube which was carefully inserted in a 1/16-inch-diameter hole drilled perpendicular to the long axis of the specimen. Temperature was then measured by means of a manually recorded potentiometer. In the beginning, it was hoped that thermocouples would only be employed initially to calibrate a system under study and that subsequent runs could be made without thermocouples using power input as a measure of temperature. Such a procedure would shorten the time necessary in performing an experiment and would remove possible sources of contamination. This technique worked well early in the program, but as experiments progressed it was found that some variation existed in the plot of temperature vs power input from sample to sample in some systems. Where this condition was encountered, thermocouples were used in all runs on that system.

Although the program was planned to uncover nonreversible changes, it was hoped that by plotting thermocouple data, some added information might be gained as to allotropic transformations, reactions, etc., occurring during the course of a run. However, a careful study of the temperature data obtained indicated that the method used was insensitive to such changes.

The highest purity starting materials obtainable were used in all systems studied. In the initial experiments solid samples were used. However, when pressure vessel failures were encountered with these materials, pre-pressed powder samples were substituted in an effort to correct the problem. As the program progressed with no further difficulty, solid samples were once again used with good success.

Powder samples were weighed, blended for 4 hours at 60 rpm under argon, pressed to the correct size at 15 tsi, and stored under argon prior to use. Solid samples were pre-cast in a multihearth arc furnace. The "buttons" were melted at least twice under argon to ensure homogeneity, and dummy titanium samples were included in each run as getters during melting.

The results of the experiments were analyzed by x-ray diffraction, light and electron microscopy, Rockwell hardness, microhardness, etc., with x-ray diffraction and metallography being the principal tools of analysis.

A General Electric XRD-3 diffractometer and a 14.32 cm Debye-Scherrer powder camera were employed for x-ray diffraction analysis, with the selection of the target material depending on the system under study. Where possible, the specimens were analyzed in the same condition as they came from the pressure cell, with only light grinding and etching necessary to remove reaction products at the specimen surfaces. Chemical analyses were usually not made, the analysis being taken as that of the sample as mixed. Since the high pressure runs frequently resulted in laminated specimens, a fresh surface could be easily examined with a minimum of specimen preparation. Typical specimens before and after pressure treatment are shown in Fig. 1.

Because of the nature of the pressure equipment used it was impossible to conduct experiments in the pressure vessel at atmospheric pressure. Therefore, where control specimens made at atmospheric pressure were deemed necessary for comparison purposes, these were heat treated in a muffle furnace at the required temperature and water quenched. In cases where powder samples were used in the high pressure runs, control experiments were made with high-purity cast alloys of the same compositions. These controls were considered valid for detecting gross changes in the pressure-treated

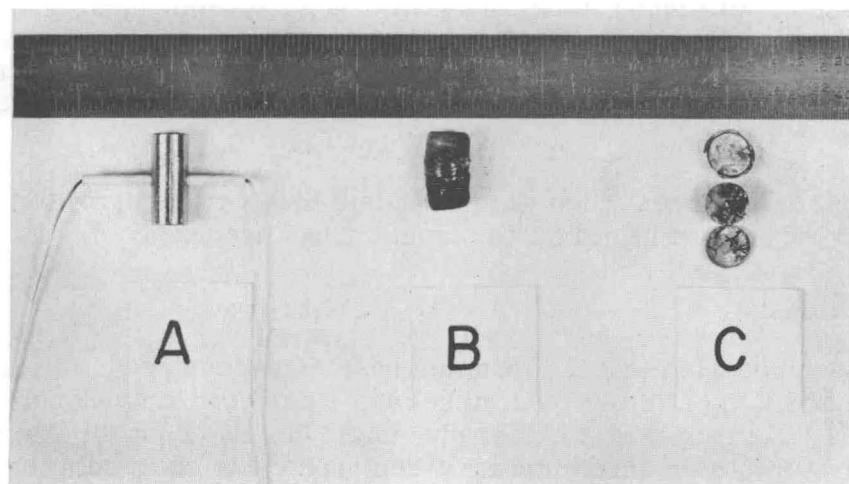


Fig. 1 Pressure samples. (A) Specimen ready for pressure run with Pt/Pt-Rh thermocouple and alumina insulating tube, but without other cell components. (B) Specimen after pressure run. Severely deformed but intact. (C) A specimen which was severely laminated during pressure run.

specimens, but it was apparent that they would not be suitable for detecting slight changes in solubility, etc., because of the different starting materials used.

In all, more than 200 runs were made and analyzed at the Metallurgical Products Department during the course of the project, with 150 of these at high pressures and temperatures.

In some systems, only a few runs were necessary to draw a conclusion, whereas with others many runs were needed.

### III. EXPERIMENTAL RESULTS

#### Investigations on the Formation or Stabilization of Phases

##### Chromium

Chromium has commanded considerable attention in recent years because of its resistance to oxidation and because of its relatively high melting point. In its usual body-centered cubic form, however, it is extremely brittle at room temperature and it is therefore limited in its use as a structural material. There is some evidence for a transformation from body-centered cubic to the face-centered cubic structure just below the melting point, (2) and in this form it should be considerably more ductile. Chromium is of particular interest as a subject for high-pressure research because the transition from body-centered cubic to the denser face-centered cubic form is favored by pressure.

Seven runs were made at 50,000 atm pressure and temperatures of 1800° to 2400°C on a sample of high-purity chromium containing 0.019 per cent nitrogen as the principal impurity.

Analysis by x-ray diffraction showed that no nonreversible transformations had occurred. All patterns showed the typical reflections for body-centered cubic chromium.

The lattice parameter was found to be 2.884 Å, in good agreement with that reported by Swanson and Tatge (2.8839 Å).<sup>(3)</sup> In the sample heated to 2400°C, extensive reaction with the Al<sub>2</sub>O<sub>3</sub> liner occurred and metallographic examination of this sample showed three or more phases present with acicular platelets and globular oxides predominating in a chromium matrix.

Nothing was observed which would indicate that a transformation from body-centered cubic to the face-centered cubic structure had occurred.

### Chromium-Nickel

It has been reported that a chromium base face-centered cubic alloy can be stabilized by the addition of 30 per cent nickel and 1 per cent molybdenum.<sup>(4)</sup> Moreover, Stein and Grant<sup>(5)</sup> have proposed a binary chromium-nickel constitutional diagram showing a high temperature, high chromium face-centered cubic solid solution field extending to about 30 wt per cent nickel. Efforts to stabilize such a phase without alloy additions have been unsuccessful. It was thought that applications of pressure and temperature might produce a stable face-centered cubic chromium solid solution containing 5 to 20 wt per cent nickel without other alloy additions.

Accordingly, four runs were made at 50,000 atm pressure at 1650°, 1750°, 1850°, and 2000°C on 95-5 and 80-20 chromium-nickel alloys. Examination by x-ray diffraction showed all samples possessed a single-phase body-centered cubic structure with the following lattice parameters:

95-5 chromium-nickel = 2.882 Å

80-20 chromium-nickel = 2.887 Å

Thus, no evidence was found for a stable face-centered cubic structure in the chromium-nickel system containing from 0 to 20 per cent nickel.

### Iron-Chromium

In the iron-chromium system, a face-centered cubic phase known as the gamma phase reportedly extends into a body-centered cubic region up to 12.5 per cent chromium between temperatures of about 900° to 1400°C. This is known as the gamma loop. Thus, iron-chromium represents a system in which both the face-centered cubic and the body-centered cubic phases are known to exist. Moreover, in the phase diagram, the two phases border upon one another. If pressure has any appreciable effect on the transformation from body-centered cubic to the denser face-centered cubic structure, the gamma loop should be displaced to compositions above 12.5 per cent chromium under the influence of pressure.

An attempt to calculate the extent of the gamma loop displacement under pressure was unsuccessful, however, because the exact extent of the loop at atmospheric pressure is still subject to much doubt, probably because of the effect of impurities and because of the sluggishness of the transformation - (see the following report on the iron-aluminum system for a type of calculation which may be carried out in fixing the gamma loop shift with pressure).

Samples of composition 10, 12.5, 15, and 20 wt per cent chromium were cast. Sections were submitted for carbon analysis and found to contain 0.03 per cent carbon.

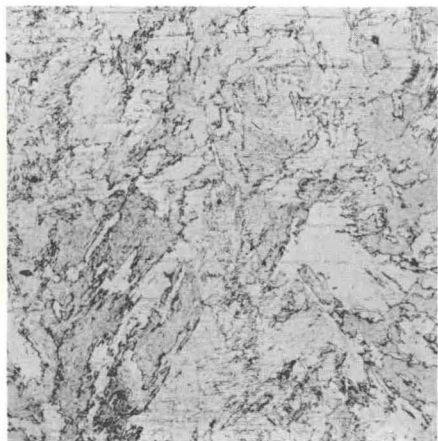
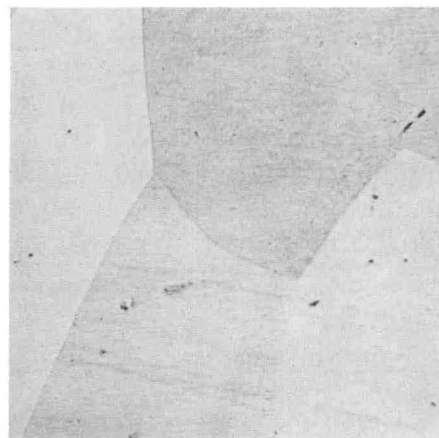


Fig. 2 Iron-(10 wt per cent chromium). Quenched after holding for 30 minutes at 1100°C, atmospheric pressure. 100X

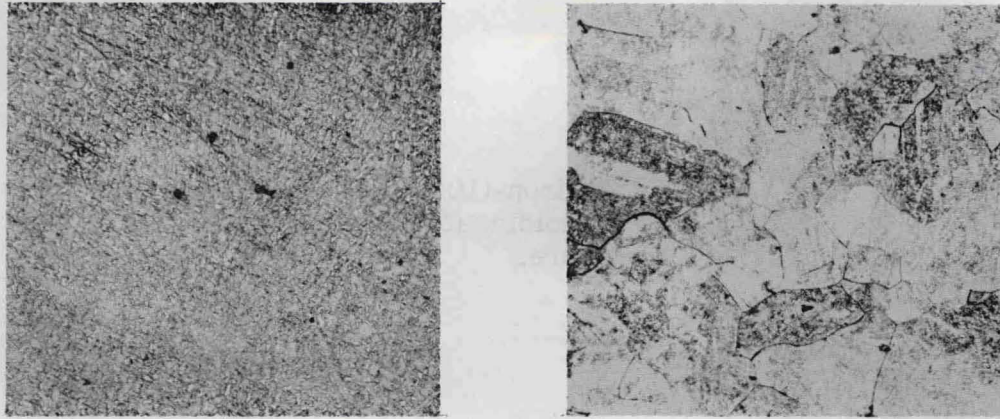
Fig. 3 Iron-(12.5 wt per cent chromium). Quenched after holding for 30 minutes at 1100°C, atmospheric pressure. 100X



Specimens were heated to 1000°, 1100°, and 1200°C at atmospheric pressure and at 100 kilobars pressure and were subsequently quenched. Carbon analyses following the pressure treatments showed no change in carbon content.

Microscopic examination of the specimens treated at atmospheric pressure revealed a refined pseudo-martensitic structure (Fig. 2) for the 10 per cent chromium composition, whereas examination of the 12.5, 15, and 20 per cent chromium compositions showed a coarse-grained, single-phase structure (Fig. 3). This may be taken as an indication of the formation of the gamma loop up to about 10 to 12.5 per cent chromium which is in agreement with that reported by Adcock<sup>(6)</sup> in his work on determining the position of the gamma loop in the iron-chromium system.

In the specimens treated at 100 kilobars, the pseudo-martensitic structure was observed in all specimens except the 20 per cent chromium composition and this had a two-phase structure (see Fig. 4). To determine if the coarse-grained, single-phase structure would be obtained above 20 per cent chromium under pressure, 22.5 and 25 per cent chromium compositions were prepared. Subsequent analysis indicated that these contained 0.02 per cent carbon and as such were essentially comparable to the 10 to 20 per cent compositions prepared previously. The specimens were treated at 1200°C under atmospheric and under 100 kilobars pressure. Microscopic examination revealed that all these specimens had the coarse-grained, single-phase structure similar to that shown in Fig. 3. Thus on the basis of the observed microstructural changes with pressure described above and summarized in the following table, it can be concluded that the



(a)

(b)

Fig. 4 (a) Iron-(20 wt per cent chromium). Quenched after holding for 30 minutes at 1100°C, 100,000 atm. (b) Iron-(10 wt per cent chromium). 100X

application of pressure had shifted the gamma loop from about 12 to about 20 per cent chromium and that the two-phase structure noted at 20 per cent chromium probably represented the  $\alpha + \gamma$  region. (This is illustrated in the phase diagram shown in Fig. 5.)

<u>Wt % Chromium</u>	<u>Treated at Atmospheric Pressure</u>	<u>Treated at 100,000 Atm Pressure</u>
10	Pseudo-martensitic structure	Pseudo-martensitic structure
12.5	Coarse-grained, single-phase	Pseudo-martensitic structure
15	Coarse-grained, single-phase	Pseudo-martensitic structure
20	Coarse-grained, single-phase	Two-phase structure
22.5	Coarse-grained, single-phase	Coarse-grained, single-phase
25	Coarse-grained, single-phase	Coarse-grained, single-phase

This conclusion is substantiated by the hardness data given below which show higher hardness values for the pressure-treated specimens in the range from about 12 to about 20 per cent chromium which represents the gamma loop shift indicated above.

Rockwell "A" Hardness Values of Specimens Prepared at Atmospheric Pressures and at 100 Kilobars

			<u>100,000 Atm</u>	<u>Atmospheric Pressure</u>
90	Fe--10	Cr	58 RA	54.5
87.5	Fe--12.5	Cr	61	35.5
85	Fe--15	Cr	61	37.0
80	Fe--20	Cr	64.5	44.0
77.5	Fe--22.5	Cr	52	45.0
75	Fe--25	Cr	52	53.0

Although it is known that both cold-work and nitrogen additions could result in grain refinement in alloys of this type, lack of an appreciable hardness difference in the 10 per cent chromium composition indicates that the effects of cold-work or nitrogen do not account for the differences in the higher chromium compositions.

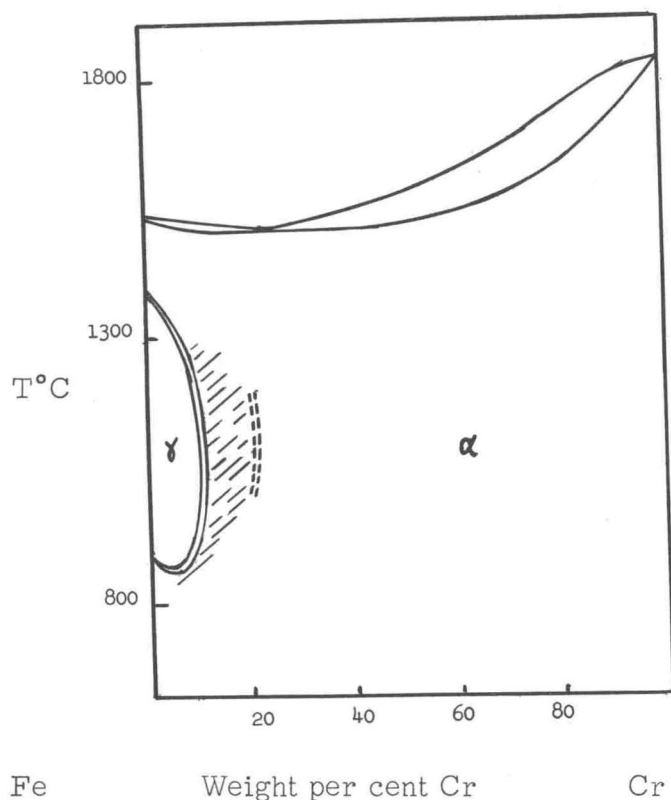


Fig. 5 Phase diagram of the iron-chromium system. Shaded area indicates the gamma-loop shift at 100,000 atm pressure.

Thus, it appears very probable that the gamma loop has been shifted to higher chromium compositions by the application of pressure. A practical application of such a shift in the gamma loop lies in the possibility of utilizing alloy additions together with pressure to produce a hardenable high-chromium alloy.

#### Iron-Aluminum

The iron-aluminum system is analogous to the iron-chromium system in that it possesses a gamma loop region reportedly extending into the body-centered cubic portion of the phase diagram to about 0.6 per cent aluminum.<sup>(7)</sup> Application of pressure at temperature could be expected to extend the gamma loop region to higher aluminum contents, and thus provide the basis for hardenable iron-aluminum alloys containing more than 0.6 per cent aluminum.

Samples of 0.5, 1.0, and 2 wt per cent aluminum in iron were prepared from cast buttons containing 0.03 per cent carbon and heat treated at 1150° and 1250°C for 30 minutes under 100 kilobars pressure and quenched. Control samples were also prepared from the same material and heat treated as above at atmospheric pressure and water quenched. As in the iron-chromium system, analysis of pressure-heat treated compositions showed no change in carbon content.

Metallographic examination of all specimens of this series subjected to pressure showed a refined spiky, pseudo-martensitic structure (Fig. 6), which could be regarded as indicative of the presence of the gamma phase at higher temperatures as noted in the previous work on the iron-chromium system. Examination of control specimens heat treated at atmospheric pressure showed a single-phase structure of very large grain size, but with some slight grain refinement noted in the 0.5 per cent aluminum sample. Fine spots were noted in the structures of all samples. These were identified as etch



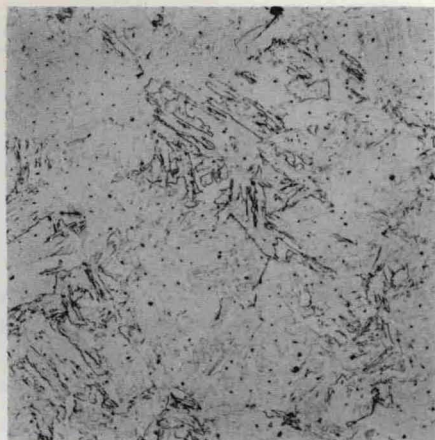


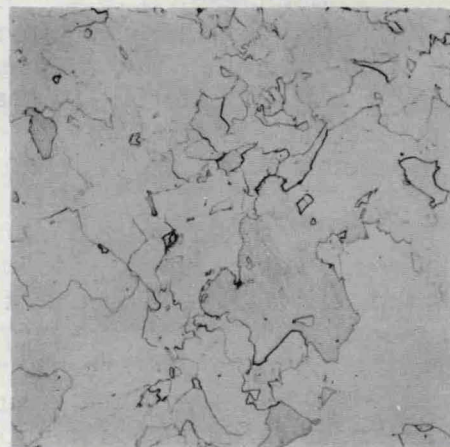
Fig. 6 Iron-(2 wt per cent aluminum). Quenched after holding at 1150°C, 100,000 atm. Etch: 2 per cent Nital. 100X

pits. Some inclusions were also detected in the pressure-treated samples which might have been the result of reaction of the specimen with the  $Al_2O_3$  liner materials.

Since a pseudo-martensitic structure was detected in all pressure-treated samples, it was thought that a gamma loop shift to aluminum contents of above 2 per cent was probable under pressure. However, the data were considered inconclusive because the 0.5 per cent aluminum control did not exhibit a pseudo-martensitic structure as expected on the basis of the reported phase diagram. Moreover, more conclusive evidence for the gamma loop shift would have been obtained if compositions had also been selected beyond the gamma loop region where a single-phase structure would have been observed. Consequently, additional compositions of 0.25, 2.25, 2.50, and 3.0 wt per cent aluminum in iron were prepared and heat treated at 1150°C under 100 kilobars and atmospheric pressure to further investigate the system. Chemical analysis of these compositions showed them to contain 0.01 per cent carbon, which is lower than the 0.03 per cent carbon materials previously employed.

Metallographic examination of these compositions showed essentially the same structures noted in the previous compositions. All the pressure-treated samples exhibited a pseudo-martensitic structure, and the conventionally treated samples showed a large-grained, single-phase structure, although the 0.25 per cent aluminum control did possess the more refined grain size as previously noted in the 0.5 per cent aluminum control. However, the 0.25 per cent aluminum control (Fig. 7) still did not have the

Fig. 7 Iron-(0.25 wt per cent aluminum). Quenched after holding for 30 minutes at 1150°C atmospheric pressure. Etch: 2 per cent Nital. 100X



martensitic structure that is believed to be indicative of the austenite to ferrite transformation.

Hardness measurements, as listed below, indicated a consistently higher hardness in all pressure-treated specimens, which might be taken as an indication of the formation of a martensite-type phase. Moreover, the hardness of the 0.25 per cent aluminum control was higher than the other control compositions which might be an indication of incipient martensite formation.

Rockwell "A" Hardness Values of Iron-Aluminum Specimens  
Prepared at Atmospheric Pressure and at 100,000 Atm

		<u>100,000 Atm</u>	<u>Atmospheric Pressure</u>
99.75	Fe--0.25 Al	56.0 R <sub>A</sub>	37.0 R <sub>A</sub>
99.5	Fe--0.5 Al	56.0	27.8
99.0	Fe--1.0 Al	55.5	29.0
98.0	Fe--2.0 Al	56.0	31.5
97.75	Fe--2.25 Al	57.0	35.0
97.5	Fe--2.50 Al	56.0	36.0
97.0	Fe--3.00 Al	56.0	38.0

Observed Microstructures  
Iron-Aluminum System

<u>Composition (wt %)</u>	<u>100,000 Atm</u>	<u>Atmospheric Pressure</u>
99.75 Fe--0.25 Al	Pseudo-martensitic	Very refined, single-phase
99.50 Fe--0.5 Al	Pseudo-martensitic	Refined, single-phase
99.0 Fe--1.0 Al	Pseudo-martensitic	Coarse-grained, single-phase
98.0 Fe--2.0 Al	Pseudo-martensitic	Coarse-grained, single-phase
97.75 Fe--2.25 Al	Pseudo-martensitic	Coarse-grained, single-phase
97.5 Fe--2.50 Al	Pseudo-martensitic	Coarse-grained, single-phase
97.0 Fe--3.00 Al	Pseudo-martensitic	Coarse-grained, single-phase

Although there appeared to be strong evidence for a gamma loop shift under pressure to compositions above 3.0 wt per cent aluminum, the failure to produce identical microstructures well inside the known gamma loop has cast some doubt on the results. It is interesting to note, however, that these experimental results agree with the following calculations by Dr. John E. Hilliard\* on the gamma loop shift to be expected under 100 kilobars pressure in the iron-aluminum system.

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## The Displacement of $\alpha$ $\gamma$ -loop With Pressure

Let  $C^\alpha$  and  $C^\gamma$  be the mol fraction of solute in the  $\alpha$  and  $\gamma$  phases in equilibrium at  $\alpha$  temperature  $T_e$ . (See Fig. 8.)

It is easily shown that, providing  $C^\alpha \ll 1$ ,

$$RT_e \left( \frac{\partial C^\alpha}{\partial P} \right)_T (\text{T.F.}) \cong \frac{C^\alpha(1 - C^\alpha)}{(C^\gamma - C^\alpha)} \{V^\gamma - V^\alpha\}, \quad (1)$$

and

$$RT_e \left( \frac{\partial C^\gamma}{\partial P} \right)_T (\text{T.F.}) \cong \frac{C^\gamma(1 - C^\gamma)}{(C^\gamma - C^\alpha)} \{V^\gamma - V^\alpha\} \quad (2)$$

where  $V^\gamma$  and  $V^\alpha$  are the molar volumes of pure gamma and alpha iron, and

$$(\text{T.F.}) = \left[ 1 + \frac{\partial \ln f_2}{\partial \ln C} \right]$$

where  $f_2$  is the activity coefficient of the solute in  $\alpha$  or  $\gamma$ . If Henry's law is obeyed (as will be the case for sufficiently small values of  $C^\alpha$  and  $C^\gamma$ ) then  $(\text{T.F.}) = 1$ .

It will be noted that the derivatives given by equations (1) and (2) are independent of the nature of the solute. It is only necessary to know  $C^\alpha$ ,  $C^\gamma$ ,  $V^\alpha$ , and  $V^\gamma$ .

### Calculation for the Fe-Al System

We wish to establish the position of the  $\gamma$ -loop at 100 k-atm. We will do this by calculating the terminal points A and B, and the values of  $C^\gamma$  and  $C^\alpha$  for  $T_e = 1150^\circ\text{C}$  (which is approximately the temperature at the maximum extension of the loop.) (See Fig. 9.)

#### A. Point B ( $\gamma \rightarrow \alpha$ in pure Iron)

According to the recent results of Claussen, (8) the transformation in pure iron occurs at a temperature of  $605^\circ\text{C}$  at 100 k-atm.

#### B. Point A ( $\delta \rightarrow \gamma$ in pure Iron)

There is apparently no experimental data for the pressure dependence of the  $\delta \rightarrow \gamma$  transformation. We can attempt to calculate it from Clapeyron's equation

$$\frac{dT_e}{dP} = \frac{\Delta V}{\Delta S} \quad (3)$$

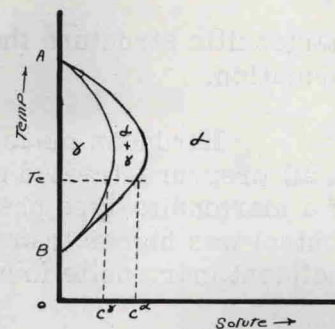
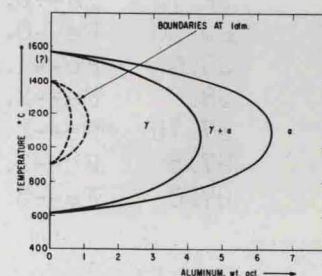


Fig. 8



CALCULATED POSITION OF THE GAMMA LOOP IN THE IRON-ALUMINUM SYSTEM AT 100 k-atm.

Fig. 9 Calculated position of the gamma loop in the iron-aluminum system at 100 k-atm.

According to the x-ray data of Basinski *et al.*,<sup>(9)</sup>  $\Delta V = 0.04 \text{ cm}^3$  per mole. From Kelley<sup>(10)</sup> we obtain  $\Delta S = 0.07 \text{ cal per deg. per mole}$ . Substituting these values in Eq. (3), we find

$$\frac{dT_e}{dP} = 0.57 \text{ deg. cm}^3 \text{ cal}^{-1} = 13.8^\circ\text{C per k-atm.}$$

If the  $\delta \rightarrow \gamma$  curve had this slope, it would intersect the fusion curve of iron [as determined by Strong<sup>(11)</sup>] at about 11 k-atm. However, Strong found no evidence of a triple point. It therefore appears that the value of  $\Delta V$  or  $\Delta S$  we have used is in error, and that the calculated  $dT_e/dP$  is unreliable. In short, we cannot locate the point A. In the accompanying figure it has arbitrarily been placed at  $1570^\circ\text{C}$ .

### C. $C^\alpha$ and $C^\gamma$ at $1150^\circ\text{C}$

According to the Fe-Al phase diagram at atmospheric pressure given by Hansen,

$$\text{and } \left. \begin{array}{l} C^\gamma = 0.012 \\ C^\alpha = 0.020 \end{array} \right\} \text{ at } T = 1150^\circ\text{C, } P = 1 \text{ atm.}$$

We now have to estimate  $V^\alpha - V^\gamma$ . Again we run into an ambiguity. The molar volume versus temperature curve determined by Basinski<sup>(9)</sup> for  $\alpha$ -iron does not extrapolate to curve for  $\delta$ -iron but, instead, intersects the curve for  $\gamma$ -iron at about  $1300^\circ\text{C}$  - which seems improbable. If the best smooth curve is drawn through the data for  $\delta$  and  $\alpha$ -iron, we obtain a value for  $(V^\alpha - V^\gamma)$  of  $0.05 \text{ cm}^3$  at  $1150^\circ\text{C}$ . We will use this value, keeping in mind that it is subject to a considerable uncertainty.

Substituting the aforementioned parameters in Eqs. (1) and (2) and assuming that they are independent of temperature and pressure we can calculate the displacement of the loop at 100 k-bars by a numerical integration. We thus obtain:

$$C^\gamma = 0.085 \text{ (= 4.4 wt pct.)}$$

$$C^\alpha = 0.12 \text{ (= 6.4 wt pct.)}$$

at  $T = 1150^\circ\text{C}$ , and  $P = 100 \text{ k-bars}$ .

Thus, Dr. Hilliard's work indicates that the gamma loop should be shifted to 4.4 per cent for the gamma phase and 6.4 per cent for the limit of the  $\alpha + \gamma$  region under 100 kilobars pressure. Since the larger values were employed for the various constants involved, and since several simplifying assumptions were necessary in the calculation, Dr. Hilliard estimates the results could easily be in error by a factor of two.

The above calculations, therefore, qualitatively confirm the experimental results reported above. Further experimental work is planned on compositions beyond 3 wt per cent aluminum to determine the actual extent of the gamma loop shift under pressure.

## Investigations of Phase Stabilization

### Chromium-Nickel (sigma phase)

The sigma phase has been detected in several binary systems including iron-chromium, cobalt-chromium, iron-vanadium, etc., Sully<sup>(12)</sup> and others have postulated an "excessive electron-atom ratio" theory to predict its occurrence in transition series alloys. To date, the sigma phase has been found at the approximately predicted composition in all systems except chromium-nickel.

Beck and Manly, <sup>(13)</sup> in work on the cobalt-chromium-nickel ternary phase system, reported that the sigma phase approaches the chromium-nickel binary system at approximately 33 atom per cent nickel at 1200°C. While there is reason to suspect the formation of sigma phase in chromium-nickel under some conditions, there is no known reason for expecting that pressure would favor its formation. However, it was hoped that application of high pressure with temperature would provide the conditions required to form the sigma phase in the chromium-nickel system.

Compositions of 60-40, 62-38, 65-35, 67-33, and 70-30 wt per cent chromium-nickel were run at 100,000 atm and the following temperatures:

1600°C for 10 minutes

1600°C for 10 minutes, followed by 20 minutes at 1200°C

1600°C for 10 minutes, followed by 20 minutes at 600°C

Metallographic examination showed the presence of two phases. X-ray diffraction studies indicated that these phases were chromium and nickel solid solutions. Sigma phase was not detected by those methods in any of the samples analyzed.

### Nickel-Copper

The ordered compounds Ni<sub>3</sub>Fe, Ni<sub>3</sub>Mn, and Ni<sub>3</sub>Co have been reported in their respective systems.<sup>(14)</sup> The ordered compound Ni<sub>3</sub>Cu has never been reported. It was felt that this compound might be stabilized under high pressures and temperatures. Two samples of composition Ni<sub>3</sub>Cu were melted at 1600°C under 100,000 atm pressure, cooled to 1000°C, held isothermally for 30 minutes and quenched under pressure. Metallographic and x-ray diffraction studies indicated that both specimens had the typical face-centered cubic solid solution structure with a lattice parameter of 3.557 Å. No evidence was found for the presence of the ordered compound, Ni<sub>3</sub>Cu.

There are also indications of incipient formation of nickel-copper under ordinary pressures up to 450°C.<sup>(15)</sup> It was hoped that the application of pressure would cause the formation and stabilization of this compound. Accordingly, cast samples of composition nickel-copper were heat treated at 450°C for 30 minutes at 100,000 atm pressure. Examination of these specimens also indicated that a typical face-centered cubic solid solution structure ( $a_0 = 3.569$  Å) was present.

### Cobalt-Aluminum

The compound Co<sub>3</sub>Al is not known in the cobalt-aluminum system, although Hansen<sup>(16)</sup> reports some indication that it may occur as a transition phase. The ordered body-centered cubic cobalt-aluminum is known, and the isomorphous compound nickel-aluminum and Ni<sub>3</sub>Al are recognized in the nickel-aluminum system. Co<sub>3</sub>Al should

possess utility in cobalt base alloys. The counterpart of  $\text{Co}_3\text{Al}$ ,  $\text{Ni}_3\text{Al}$ , is recognized as the most important single compound in nickel base high-temperature alloys because (1)  $\text{Ni}_3\text{Al}$  is the major dispersed phase, (2) it possesses the dense ordered face-centered cubic structure, and (3) it is coherent with the matrix. For the same reasons, cobalt alloys could be rendered more useful if the dense compound  $\text{Co}_3\text{Al}$  were formed under pressure.

The stoichiometric composition  $\text{Co}_3\text{Al}$  was prepared from high-purity powders and melted by holding at  $1600^\circ\text{C}$  for 20 minutes at pressures of 50,000 and 100,000 atm. In addition, samples were cast under the above pressures and then isothermally held at  $1200^\circ$  and  $1250^\circ\text{C}$  to ascertain the effects of heat treatment under pressure. These materials were compared with samples heat treated at atmospheric pressure.

Metallography showed identical structures for both modes of treatment indicating that pressure had no beneficial effect in synthesizing the  $\text{Co}_3\text{Al}$ . X-ray diffraction showed the presence of two phases, identified as cobalt-aluminum and beta-cobalt (Table I).

TABLE I

X-RAY DIFFRACTION ANALYSIS

Cobalt-Aluminum System-- $\text{Co}_3\text{Al}$  Composition

Molybdenum K Radiation	<u>d/n</u>	<u>I/I<sub>0</sub></u>	<u>Identification</u>
	2.17	VW	$\beta$ -Cobalt
	2.03	S	$\beta$ -Cobalt
	1.92	MS	$\beta$ -Cobalt
	1.46	VW	$\beta$ -Cobalt
	1.275	W	Aluminum-Cobalt
	1.265	W	$\beta$ -Cobalt
	1.170	MS	Aluminum-Cobalt
	1.07	W	$\beta$ -Cobalt
	1.05	VVW	$\beta$ -Cobalt
	1.01	M	Aluminum-Cobalt

Chromium-Aluminum

The intermetallic compound chromium-aluminum is not found in the chromium-aluminum system. However, the high melting compounds cobalt-aluminum and nickel-aluminum are present in their respective systems. It is postulated that chromium-aluminum might be formed under high pressures, and that this compound should possess a melting point substantially above either of its constituents.

TABLE II  
X-RAY DIFFRACTION ANALYSIS

Chromium-Aluminum System--CrAl Composition

Molybdenum K Radiation

<u>Cast at Atmospheric Pressure</u>		<u>Cast--100,000 Atm Pressure</u>	
<u>d/n</u>	<u>I/I<sub>0</sub></u>	<u>d/n</u>	<u>I/I<sub>0</sub></u>
--	--	2.58	VVW
2.42	M	2.42	W
2.16	S	2.16	S
1.98	VW	1.98	W
1.95	VVW	1.94	VVW
1.86	VW	1.84	VVW
1.64	VVW	--	--
1.52	W	1.54	VW
1.47	VW	1.46	VVW
1.40	VW	--	--
1.35	VW	--	--
1.32	M	1.33	M

Stoichiometric proportions of chromium and aluminum were heated to 1900°C under pressures of 50,000 and 100,000 atm. The resulting cast specimens were so friable that they could not be prepared for metallographic examination. However, the major reflections in the x-ray diffraction patterns (Table II) were found to be the same as those given by samples of the same composition melted at atmospheric pressure.

A further effort was made to clarify the chromium-aluminum system by studying compositions of 80-20, 85-15, and 70-30 chromium-aluminum under pressure, but because of the complexity and quality of the diffraction patterns obtained it was decided that the specimens did not warrant the extended study that would be required.

Investigations of Intermediate Phase Suppression

Nickel-Aluminum

The phase diagram for nickel-aluminum shows that the ordered compound Ni<sub>3</sub>Al forms as the result of the peritectic reaction between nickel-aluminum and the melt. Consequently, in synthesizing this compound, severe peritectic segregation usually occurs, which necessitates long-time, high-temperature annealing treatments for homogenization. Such treatment normally results in large grain size which is detrimental to physical properties. It is postulated that since the peritectic occurs so close to the liquidus,

casting under pressure may modify the mode of nucleation and cause  $\text{Ni}_3\text{Al}$  to form congruently from the melt, thus avoiding peritectic segregation.

Experiments were run in which melts of composition  $\text{Ni}_3\text{Al}$  were cooled quickly from  $1600^\circ\text{C}$  under pressures of 50,000 and 100,000 atm. Metallographic examination of the specimens so obtained showed a two-phase structure indicating that the peritectic reaction had still occurred (Fig. 10). A third experiment was run in which the melt was cooled to  $1300^\circ\text{C}$  and held isothermally for 30 minutes to cause homogenization of the  $\text{Ni}_3\text{Al}$ . Metallographic examination indicated that although homogenization was not complete, the usual very large grains were substantially formed. It seems likely though the evidence is meager, that the application of pressure up to 100,000 atm under these conditions will not cause  $\text{Ni}_3\text{Al}$  to form congruently from the melt.

#### Nickel-Titanium

Nickel alloys with additions of 15 wt per cent titanium or less are not forgeable. An examination of this region in the phase diagram shows the presence of the hexagonal intermetallic  $\text{Ni}_3\text{Ti}$  and a solid solution of titanium in nickel. This alloy was to be prepared under pressure in the hope that the solubility of titanium may be increased and that the formation of  $\text{Ni}_3\text{Ti}$  might either be suppressed or that it might be precipitated in a cubic form analogous to  $\text{Ni}_3\text{Al}$  rather than in its usual form of hexagonal needles.

Runs were made on powder samples of 80-20, 85-15, and 90-10 wt per cent nickel-titanium alloys at 50,000 atm pressure and at temperatures of  $1300^\circ$ ,  $1350^\circ$ ,  $1400^\circ$ , and  $1450^\circ\text{C}$ . The samples were held at temperature for 10 minutes and quenched. These temperatures were below the melting point, and diffusion was not sufficient to produce equilibrium structures. The experiments were therefore repeated at  $1600^\circ\text{C}$  to produce cast structures.

Metallographic comparison of the high pressure runs with duplicating runs made at atmospheric pressure showed no detectable changes. X-ray examination showed that  $\text{Ni}_3\text{Ti}$  had precipitated in its normal hexagonal structure.

To ascertain if solubility changes could be produced by heat treatment under pressure, samples of a cast 90-10 wt per cent nickel-titanium alloy were heat treated at  $1000^\circ\text{C}$  at atmospheric pressure and under 50,000 atm pressure for 30 minutes, which was the maximum holding time permissible for satisfactory operation of the pressure equipment. Metallographic examination showed no apparent differences in amounts of eutectic and nickel solid solution present, indicating that no significant changes in solubility had occurred under these conditions. However, the above structures were not considered homogenous, (indeed, eutectic should not have been present if equilibrium had been attained) and if sufficient holding time could have been allowed to achieve equilibrium, a change in solubility might have been observed.

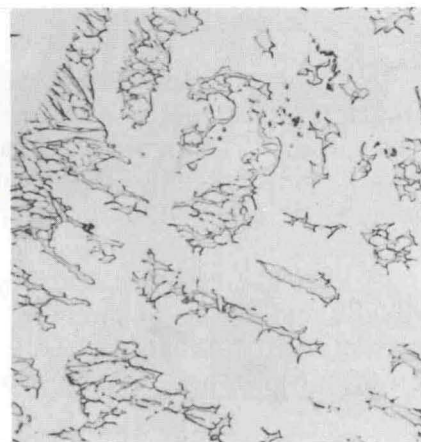


Fig. 10  $\text{Ni}_3\text{Al}$  compound. Melted at  $1600^\circ\text{C}$ , 100,000 atm and cooled under pressure. (The white field is  $\text{Ni}_3\text{Al}$  and the dark etching minor phase is nickel-aluminum.) 500X



## Nickel-Molybdenum

The inferior properties of some molybdenum-nickel alloys are due in part to the formation of the intermetallic nickel-molybdenum which sharply decreases the ductility of the alloy. In conventional techniques, this phase is suppressed by aluminum additions. It was hoped that casting various compositions of this alloy under pressure would collapse, dissolve, or otherwise suppress this intermetallic so that a ductile alloy may result.

Runs were made at 50,000 and 100,000 atm pressure and a temperature of 1600°C on 62-38 and 40-60 wt per cent molybdenum-nickel alloys. Metallographic comparison of samples with those melted at atmospheric pressure indicated that the alloys had not been affected in any way by pressure application.

### III. GENERAL STUDIES

#### Titanium-Magnesium

This system has been difficult to investigate by conventional techniques because of the great difference in volatility of the components. Because of this there is little known about the phase diagram. Aust and Pidgeon<sup>(17)</sup> reported the solubility of titanium in magnesium to be 0.0025 per cent at 650°C and 0.15 per cent at 850°C. Fredrickson<sup>(18)</sup> managed to dissolve 1.5 per cent magnesium in titanium by sheath-rolling compressed compacts. In a previous study by the General Electric Company, Oriani and Strong<sup>(19)</sup> dissolved approximately 1 per cent magnesium in titanium using high pressures (about 70,000 atm) and temperatures.

It was decided to survey the entire titanium-magnesium system using high pressures in order to ascertain the solubility of the components and to search for any intermediate phases in the system. Accordingly, powder compositions of 90-10, 70-30, 50-50, 30-70, and 10-90 wt per cent titanium and magnesium were prepared using high-purity atomized magnesium and sodium reduced titanium powders.

Initially, runs were made at 50,000 atm pressure and temperatures of 800°, 1200°, and 1400°C for 10 minutes. In addition, samples of the 90-10 wt per cent titanium-magnesium composition were held at 1850° to 1900°C for 10 minutes.

In the higher magnesium alloys some difficulty was initially encountered in holding the volatile component, but subsequent runs resulted in satisfactory samples.

Analysis of specimens by metallography and x-ray diffraction indicated that there were no intermediate phases in the system, and that mutual solubility of the components is very limited. X-ray diffraction examination of all compositions showed a two-phase alloy. Lattice parameter determinations on 90-10 and 10-90 wt per cent titanium-magnesium compositions indicated no change up to 1400°C where both components then showed slightly enlarged unit cells, probably indicating slight mutual solubility.

Titanium a = 2.96 A	Magnesium a = 3.215 A
c = 4.72 A	c = 5.23 A

Lattice parameters of the starting powders were as follows:

Titanium a = 2.95 A	Magnesium a = 3.21 A
c = 4.69 A	c = 5.21 A

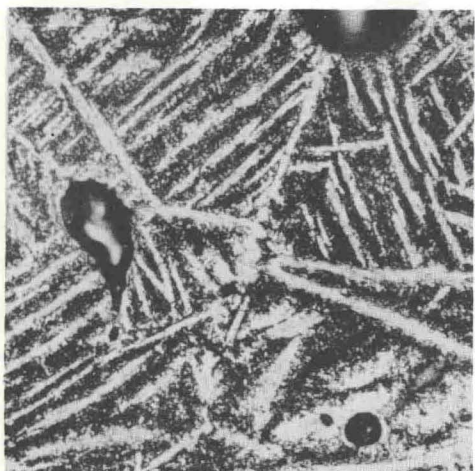


Fig. 11 Titanium-(10 wt per cent magnesium). Prepared by melting powdered components at  $1900^{\circ}\text{C}$ , 100,000 atm and cooled under pressure. (Globules of magnesium in an acicular titanium matrix.) 500X

Fig. 12 Titanium-(2 wt per cent magnesium). Prepared by melting bulk components at  $1900^{\circ}\text{C}$ , 100,000 atm and cooling under pressure. 500X



Metallographic examination of 90 titanium and 10 magnesium melted at  $1900^{\circ}\text{C}$  showed globular magnesium areas in an acicular titanium matrix (Fig. 11). As this microstructure did not agree with that found by Oriani and Strong, who worked with solid starting materials, it was decided to attempt to duplicate their work, since powders could conceivably suffer from adsorbed gases which would affect the results.

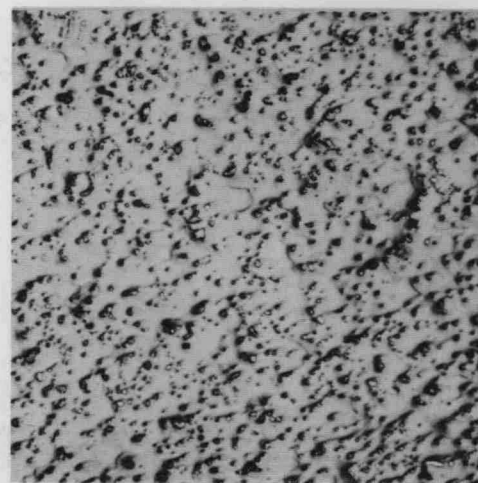
Accordingly, three cylinders of high-purity titanium were machined with 0.070-inch holes drilled in each end to receive 0.070-inch diameter extruded magnesium rod so that the final product would contain 2 per cent magnesium. The samples were then melted at  $1900^{\circ}\text{C}$  under 50,000 and 100,000 atm pressure. Examination (Fig. 12) showed all samples possessed the acicular matrix noted in the powder samples, and, moreover, the titanium and magnesium alloy exhibited a fine globular dispersion of magnesium which indicated that solubility was much less than the 2 per cent introduced. Unless one assumes the melting temperature was sufficiently high for gaseous impurities to be absorbed even in the solid sample, there is no apparent explanation for the different structures obtained in the two investigations.

As the application of high pressures in this study was primarily to contain the volatile component, it was decided to attempt to use an available vacuum hot press to make larger specimens in order to ascertain physical properties. This apparatus is capable of 200 atm pressure and temperatures of  $2000^{\circ}\text{C}$ , and possesses the advantage of more positive control of variables, particularly atmosphere.

Two cylinders 1 inch in diameter x 2 1/2 inches long of a titanium and 2 per cent magnesium composition were hot-pressed from powders at 1000°C and 200 atm pressure for 2 hours. The cylinders were then machined into tensile bars and tested. Tests were compared with pure titanium specimens prepared from the same powder batch under the same conditions. Results are as follows:

	Titanium-2% Magnesium (avg of 2)	Titanium (avg of 4)
Density	4.397 g/cm <sup>3</sup>	4.50 g/cm <sup>3</sup>
Tensile strength	70,000 psi	79,000 psi
Yield strength	50,800 psi	53,000 psi
Elongation	18.9 per cent	18.0 per cent
R. A.	21.9 per cent	23.3 per cent

Fig. 13 Titanium-(2 wt per cent magnesium). Hot pressed from powders at 1000°C, 200 atm. Un-etched, polarized light. 100X



Metallographic examination showed a fine globular dispersion of magnesium in a dense, essentially porous free, equiaxed titanium matrix (Fig. 13). Physical properties show a slight degeneration of properties from those of pure titanium. It is unknown whether changes in temperature or holding time would have improved the physical properties of this alloy. It is interesting to note, however, that the microstructure obtained was closer to that described by Oriani and Strong, so that gas absorption may have affected the results obtained in the high pressure equipment.

#### Nickel-Aluminum Oxide

Dispersion hardened alloys have been recognized as being of great importance in high-temperature applications. Unfortunately, most particles used as hardeners in present high-temperature alloys either dissolve or coarsen at service temperatures. The resulting softening and structural changes limit the useful life of the alloy. Al<sub>2</sub>O<sub>3</sub> exhibits virtually no solubility in nickel. [Cochardt<sup>(20)</sup> has calculated from thermodynamic data a solubility of  $1 \times 10^{-14}$  at 1000°K.] One of the major obstacles in the use of Al<sub>2</sub>O<sub>3</sub> as an alloy hardener has been the problem of producing fine, uniform particle dispersions. By employing the internal oxidation method of reacting nickel oxygen,

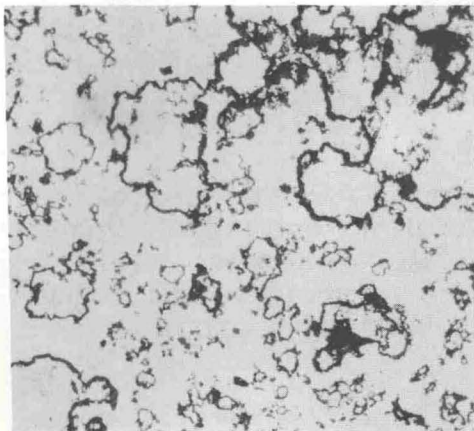


Fig. 14 Mixture of nickel oxide, 50-50 aluminum-nickel alloy, and pure nickel powders heated at 50,000 atm. Unetched. 200X

aluminum, and nickel at elevated temperatures under pressure, it was thought that a fine dispersion of  $Al_2O_3$  in nickel might be produced.

A powder mixture was made of nickel oxide, a 50-50 aluminum-nickel alloy, and pure nickel containing stoichiometric proportions of nickel oxide and aluminum such that the reacted mixture would contain 5 mol per cent aluminum oxide in nickel. Several runs were made in the temperature range  $1200^\circ$  to  $1700^\circ C$  at pressures of 50,000 atm. Metallographic and x-ray diffraction examination indicated that complete reaction did not occur until a temperature of about  $1650^\circ C$  was reached. The aluminum oxide thus formed appeared in chains and ringlets which were mostly agglomerated in the grain boundaries of the nickel matrix and at the interfaces of the former nickel-oxygen - nickel-aluminum boundaries (see Fig. 14). Lattice parameter measurements of the nickel matrix showed a lattice constant of 3.524 Å which indicates the matrix is essentially impurity free.

The dispersion of aluminum oxide was not nearly as fine as was desired. The particles were of the order of one micron in size and considerably agglomerated. Although it is realized that refinements in technique, such as reducing the particle size of the starting materials and employing extended milling for better blending, would offer some improvements, it was not seen that application of pressure offered any advantages and no additional work was performed.

#### High-speed Tool Steel

Presently, high-speed tool steels are very difficult to homogenize because of the relative insolubility of alloy carbides in the gamma phase. Efforts to homogenize in the gamma region at higher temperatures result in grain growth which is more detrimental than any improvement gained by increased carbide solubility. It was felt that austenitizing under pressure might result in increased homogeneity at equivalent or lower temperature and that tempering under pressure might retain this advantage in the final product.

A sample of super high-speed steel was obtained with the following typical analysis:

Carbon	0.77 %
Tungsten	18.5
Chromium	4.50
Vanadium	2.00
Molybdenum	1.00
Cobalt	9.00

Specimens were preheated at 1500°F for 10 minutes and then austenitized at 200°, 2300°, and 2400°F for 10 minutes at atmospheric pressure and under 100,000 atm and quenched. In addition, some of the quenched samples were tempered at 900°C and others were double tempered at 1000° and 700°F for 30 minutes at each temperature at atmospheric pressure and under 100,000 atm.

Rockwell "C" hardness determinations and metallography were the principal tools of analysis. Austenitic grain size was delineated by Vilella's reagent in all samples except those austenitized at 2000°C. Efforts to etch the 2000°F specimens with other etchants were unsuccessful. Grain size was determined by the standard intercept method at 1000X magnification.<sup>(21)</sup> Results of these studies are summarized in Table III.

TABLE III

Comparison of Grain Size and Hardness of Pressure Treated and Conventionally Treated Tool Steel

	As Quenched	Grain Size	Tempered	Grain Size	Double Temper	Grain Size
Temperature	2000°F		900°F		1000° + 700°F	
Hardness R <sub>C</sub> (exp)	61.5	N.V.*	63.0	N.V.	62.0	N.V.
Hardness R <sub>C</sub> (std)	61.5	N.V.*	63.0	N.V.	63.0	N.V.
Temperature	2300°F		900°F		1000° + 700°F	
Hardness R <sub>C</sub> (exp)	64.0	11	66	11	65	12
Hardness R <sub>C</sub> (std)	65.5	11	66	12	66	11
Temperature	2400°F		900°F		1000° + 700°F	
Hardness R <sub>C</sub> (exp)	66.0	11	63.5	8	62	5
Hardness R <sub>C</sub> (std)	62.0	3	64.0	3	62	3
Temperature	2500°C					
Hardness R <sub>C</sub> (exp)	60.0	5				
Temperature	2600°C					
Hardness R <sub>C</sub> (exp)	60.0	3				

\*Not Visible

Metallographic examination revealed that the average particle size of the alloy carbides was generally finer and their distribution was somewhat more uniform in pressure-treated specimens at all austenitizing temperatures as compared to those treated at atmospheric pressure. Moreover, a cursory examination by electron microscopy of samples quenched from 2300°F and tempered at 900°F indicated that the pressure-treated sample possesses a finer martensitic structure with some indication of a fine acicular precipitate which could not be identified (Figs. 15 and 16). Comparison of pressure-treated and conventionally treated specimens austenitized at 2300°F indicated the same average grain size, although the conventionally treated specimen was 1.5 R<sub>C</sub> harder in the as-quenched condition. However, this advantage was not retained during tempering.

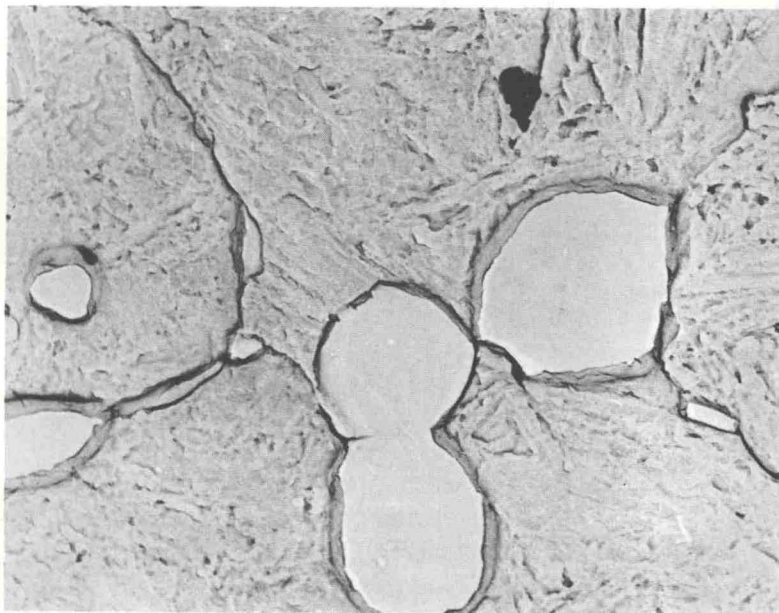


Fig. 15 High-speed tool steel.  
Heat treated at atmospheric pressure. Austenitized at 2300°F, quenched and tempered at 900°F for 10 minutes. Etch: Vilella's reagent. Electron micrograph. 5000X

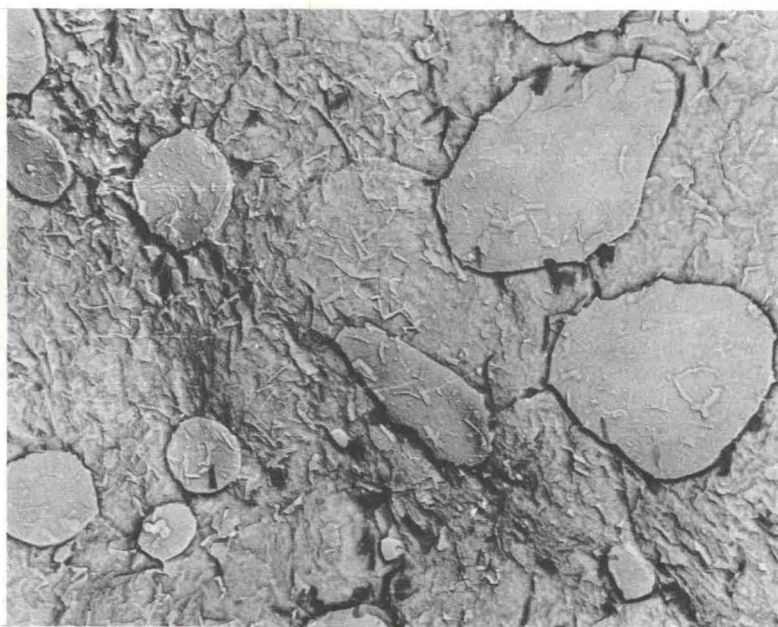


Fig. 16 High-speed tool steel.  
Heat treated at 100,000 atm pressure. Austenitized at 2300°F, quenched and tempered at 900°F for 10 minutes. Etch: Vilella's reagent. Electron micrograph. 5000X

Comparison of 2400°F treated samples is interesting as the manufacturer recommended 2350° to 2400°F as the normal austenitizing temperature for this material. The grain size of the pressure-treated specimen remained fine (ASM No. 11), whereas the grain size of the conventionally treated sample had coarsened to ASM No. 3, giving a grain size difference of about a factor of 4 (Figs. 17 and 18). Further examination showed the carbides had remained spherical and uniformly distributed under pressure, whereas, when normally treated, severe growth and coalescence of the alloy carbides at the grain boundaries had occurred. Moreover, the hardness of the pressure-treated sample had increased to 66 R<sub>C</sub> while the control dropped to 62 R<sub>C</sub> in the as-quenched condition. A single tempering at 900°F showed the standard had regained some hardness through secondary hardness effects, whereas the pressure-tempered specimen displayed no secondary effects as its hardness declined to 63.5 R<sub>C</sub>. However, the grain size of the

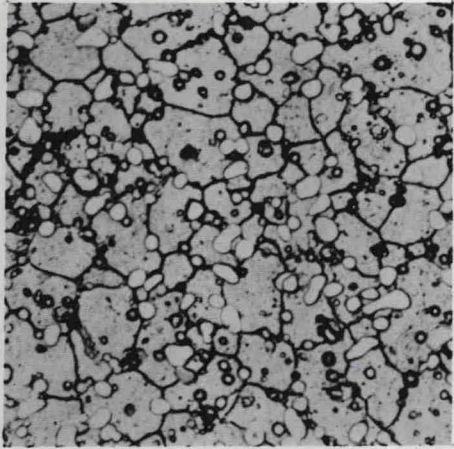


Fig. 17 High-speed tool steel. Heat treated at 100,000 atm pressure. Preheated at 1500°F for 10 minutes. Austenitized at 2400°F for 10 minutes and then quenched. 750X



Fig. 18 High-speed tool steel. Heat treated at atmospheric pressure. Preheated at 1500°F. Austenitized at 2400°F and air cooled. 750X

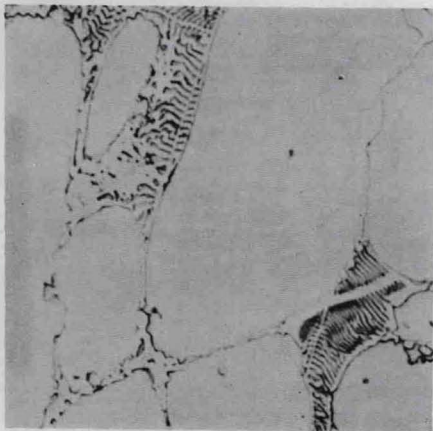


Fig. 19 High-speed tool steel. Heat treated at 100,000 atm pressure. Preheated at 1500°F for 10 minutes. Austenitized at 2600°F for 10 minutes and then quenched.

samples tempered under pressure did not remain constant, but showed increases to ASM No. 8 and ASM No. 5 for single and double drawing, respectively. As one would not expect a drawing operation to change the former austenitic grain size, the austenitic treatment of these samples must be considered questionable. However, a comparison of the largest grain sized specimen austenitized at 2400°F under pressure with normally austenitized material at the same temperature indicates that grain size remains more refined under pressure.

In order to determine the austenitizing temperature that is required under pressure to produce the structure noted in the controls austenitized at 2400°C, samples were austenitized at 2500° and 2600°F under 100,000 atm pressure for 10 minutes and quenched under pressure. Hardness of both samples fell to 60 R<sub>C</sub> and austenitic grain size increased to ASM No. 5 and ASM No. 3 at 2500° and 2600°F, respectively. Metallographic examination of the alloy carbide phase in these samples indicated that a severe "chinese script" like coalescence of the carbides had occurred at the grain boundaries at both temperatures (Fig. 19).

In summary, austenitizing under pressure has apparently raised the grain growth threshold at least 100°F. Furthermore, it appears that pressure has resulted in more positive control of particle size and distribution of complex carbides up to the grain growth temperature. Tempering under pressure has probably affected the rate of nucleation and precipitation from martensite, and the precipitate formed could be of a different nature. Pressure treatments seem to have little effect on hardness. The pressure treated samples do tend to be a little lower in hardness, however, and this may be an indication that the rate of solution of the alloy carbides has been adversely affected by pressure.

The more important variables governing the properties of tool steels include austenitic grain size and carbide distribution. In view of the effects of pressure on these variables as noted above it may be concluded that pressure treatment should have a beneficial effect on the properties of tool steel. Unfortunately, due to limitations imposed by the specimen size employed, these probable improvements could not be directly measured.

#### IV. DISCUSSION OF RESULTS

The large volume change occurring in the transformation from graphite to diamond is extremely rare, if not unique, in metal as well as in nonmetal systems. The results of this exploratory project indicate that metal systems in general are not likely to reveal highly sensational irreversible changes as a result of the application of pressure. This is in agreement with that expected in view of the elastic nature of the metallic bond and of the fact that metallic systems generally already exist as closely packed structures because of the nondirectional nature of the bond.

However, reversible, more moderate structural changes such as the transformation from body-centered cubic to the denser face-centered cubic structure, can be expected to occur as a result of the application of pressure, since these transformations occur rather readily in metal systems with moderate changes in conditions even without the application of pressure. Thus, strong evidence was found in the iron-chromium and iron-aluminum systems to indicate that the face-centered cubic ( $\gamma$ ) region was extended to higher alloy contents by the application of pressure. The fact that a similar reversible transformation was not detected in pure chromium or chromium-nickel alloys does not indicate, of course, that it has not occurred, since in these cases transformation products indicative of a reversible change may not have been produced or retained. The effects of pressure noted on high-speed steel may have been due more to the effects of pressure on the kinetics of the system rather than on phase transformations directly.

Although these transformations may not involve vastly different structures, it should be recognized that they may be the basis for significant property improvements. Unfortunately, interest in the practical aspects of these findings may be somewhat dampened by the inability to produce sufficiently large quantities of the alloys for more extended testing or for actual structural application. However, a continued, more careful, and more theoretical study of pressure effects may contribute significantly to our understanding of the fundamental nature of metal systems and may indirectly lead to improvements in alloys made by more conventional techniques.

#### ACKNOWLEDGMENTS

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In particular we wish gratefully to acknowledge the work of Dr. J. E. Hilliard, who prepared the calculation on the displacement of the gamma loop in the Fe-Al system under pressure.

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